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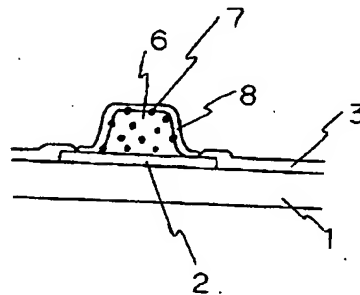
(54)【発明の名称】 突起電極の構造および突起電極の形成方法

(57)【要約】

【目的】電気素子あるいは基板上に形成した突起電極の特性を改良し、フェイスダウンボンディング等に使用する際の接続信頼性を向上させる。

【構成】半導体素子1のA1電極2上に金属粒子7を含んだ樹脂6を形成する。これを金属メッキ浴に浸漬し、樹脂6より突出した金属粒子7を核として金属膜8が成長する事により樹脂6上に金属膜8が形成され、同時にA1電極2上にも金属膜8が形成され、A1電極2上に樹脂6の層を含む突起電極が形成される。

【効果】微細なピッチでのバンプ形成が可能であり、さらに変形が容易に行えることにより平滑な基板への実装においても確実な接続を可能とする。さらに樹脂中に金属粒子を含有させることにより金属膜の形成を容易にし、金属粒子のアンカー効果により金属膜の樹脂への密着力を向上させ、高い信頼性を半導体装置に提供できる。



【特許請求の範囲】

【請求項1】 電気素子あるいは基板上の電極より突出した形状を持つ突起電極において、少なくとも前記電極上の一部を覆うように金属粒子を分散させた樹脂の層を形成し、前記金属粒子を含む前記樹脂と前記電極上にのみ金属被覆を形成したことを特徴とする突起電極の構造。

【請求項2】 電気素子あるいは基板上の電極の一部を覆うように金属粒子を分散させた樹脂の層を形成する工程と、前記電気素子あるいは前記基板を無電解メッキ浴中に浸漬し、前記電極と前記金属粒子を含む前記樹脂層上にのみ金属皮膜を形成する工程、よりなことを特徴とする突起電極の形成方法。

【請求項3】 上記金属皮膜としてNi、Co、Cu、Au等の無電解メッキ皮膜を施したことを特徴とする請求項1記載の突起電極の構造。

【請求項4】 上記金属粒子としてAu、Ni、Co、Pd、Cu、Zn、Sn、Ag等の無電解メッキ可能な金属を含む粒子を用いた請求項1記載の突起電極の構造。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、電気素子あるいは基板上に形成した突起電極の構造および形成方法に関わり、更に詳しくは突起電極の特性改良に関する。

【0002】

【従来の技術】突起電極を形成する方法として、従来電気メッキ法によって金属塊の突起電極を形成していた。

【0003】図4は、電気メッキ法で形成された突起電極を有する半導体素子の断面図である。図において、101は半導体素子、102は半導体素子101上に設けられたA1電極、103はパッシベーション膜、104はA1電極102上にNi、Cr、Pt、等の金属で形成されたバリアメタル、105はバリアメタル104上に電解メッキ法で形成された突起電極の役目を果たす金属バンプである。

【0004】次に金属バンプを形成する方法を説明する。まず、半導体素子101上にNi、Cr、Pt、等の金属を真空槽内でスパッタ法により蒸着形成する。形成した金属膜上にポリイミド系のレジストを塗布し、マスクを重ねて紫外線を照射することで、A1電極102上を除くレジストを硬化させ、未硬化のレジストを溶剤除去し、A1電極上のみ開口部を設ける。次にレジスト層を形成した半導体素子101をAuメッキ浴に付け金属膜に電圧を加える。レジストの開口部に露出している金属膜上のみAuが成長し、Auバンプ105が形成される。Auバンプ105が形成された後、レジスト層を溶剤除去し、さらに金属膜をバンプ105をマスクとしドライエッチングを施すことによりバリアメタル10

4を形成する。

【0005】

【発明が解決しようとする課題】上記のような突起電極の形成方法では、次のような問題点を有する。即ち、工程が非常に多く複雑であり真空蒸着などコストのかかる工程を数多く含むため製造単価が高くなり、またメッキ金属が半導体素子の面方向にも成長するため隣接した端子間でのショートが発生し、微細ピッチの突起電極形成が困難である。また、チップ・オン・ガラスと呼ばれている半導体素子を基板上にフェースダウンの形で実装する方法においては、高さを均一に揃えることが困難な上記突起電極では接続信頼性が著しく低下する。さらに金属塊である上記突起電極は、変形し難いためソリッドでかつ平滑な基板への対応が困難であった。

【0006】本発明は、上記の課題を解決すべくなされたもので、電極上に変形し易くかつ微細ピッチに対応した突起電極を提供することを目的としている。

【0007】

【課題を解決するための手段】本発明による突起電極の構造は、電気素子あるいは基板上の電極より突出した形状を持つ突起電極において、少なくとも前記電極上の一部を覆うように金属粒子を分散させた樹脂の層を形成し、前記金属粒子を含む前記樹脂と前記電極上にのみ金属被覆を形成したことを特徴とする。

【0008】

【作用】電極上に金属粒子を含んだ樹脂を形成する。これを金属メッキ浴に浸漬し、樹脂より突出した金属粒子を核として金属膜が成長する事により樹脂上に金属膜が形成され、同時に電極上にも金属膜が形成され、電極上に樹脂の層を含む突起電極が形成される。

【0009】

【実施例】以下、本発明による一実施例を説明する。

【0010】図1は、本発明による突起電極を有する半導体素子の断面図であり、図2は、本発明による突起電極の要部を拡大して示した断面図である。1は半導体素子、2は半導体素子1上に電気信号の入出力を行なうために設けられたA1電極、3は半導体素子1の能動面を保護するために設けられたパッシベーション膜、6はA1電極上に形成された樹脂、7は樹脂中に分散した金属粒子、8は樹脂6およびA1電極2上を覆うように形成された金属膜である。

【0011】図3(a)～図3(d)は、図1および図2に示した本発明による突起電極を形成する工程を示した断面図であり、9はマスク、10は紫外線の照射方向を示す矢印、11は樹脂6が紫外線によって硬化した領域であり、12はパラジウム皮膜である。本発明による突起電極の形成方法は、以下の通りである。

【0012】まず、半導体素子1の能動面上に金属粒子7を一樣に分散させた樹脂6をディスペンサー等を使って適量滴下する。滴下した樹脂6を半導体素子1上に均

一に広げるため、半導体素子1を約3,000rpmで10秒間の高速回転を行ない、樹脂6を約20μmの厚みとなるようにスピコートする。このとき使用した樹脂6は、液状の紫外線硬化型のポリイミド系樹脂であり、金属粒子7として粒径0.1~1μmのAg-Pd粉末を樹脂6中に5~20%含有させている。樹脂6として紫外線硬化型のポリイミド樹脂を用いたのは、パターン形成が容易に行え、なおかつ耐薬品性にすぐれているためであり、無電解メッキ液に侵されない樹脂であれば、膜状の樹脂や非感光性樹脂を用いても良い。樹脂6をスピコートした半導体素子1を8.0℃で約1時間乾燥させ、図3(a)の構造を得る。つぎに、図3(b)に示すように、半導体素子1のA1電極2に対応した位置に開口部を持つマスク9を図3(a)の半導体素子1上に位置合わせをして載せ、紫外線を矢印10の方向に照射し樹脂6を領域11のみ硬化させる。マスク9の開口部をA1電極2より小さくすることにより、樹脂6の硬化領域11はA1電極2より小さくなるよう設計されている。

【0013】樹脂6の未硬化部分を除去するため、樹脂6の現像液に半導体素子1を約2分間浸漬し、図3(c)の構造を得る。このとき、樹脂6の硬化領域11も一部エッチングされるため、樹脂6の厚みは図3(a)に示した状態より約20~30%減少する。このため図3(c)に示すように金属粒子7が樹脂6より突出した状態となる。

【0014】A1電極2上にもメッキを施すための前処理として、半導体素子1を塩化スズ(II)溶液および塩化パラジウム溶液に浸漬し、図3(d)に示すようにA1電極2上に活性化したパラジウム皮膜12を形成する。

【0015】最後に金属膜8を形成するため半導体素子1を無電解Niメッキ浴に浸漬する。A1電極2上にはパラジウム皮膜12が存在するため、無電解メッキ浴中のNiがパラジウム皮膜12と置換することによりA1電極2上に析出する。また、樹脂6上においても樹脂6の表面より突出した金属粒子7を核としNi膜が成長する。このようにして、金属粒子7を核とすることで樹脂6上に成長したNi膜と、A1電極2上に成長したNi膜とが結合し、図2に示すようにA1電極2および樹脂6を覆うように金属膜8が形成され、突起電極を形成する。金属粒子7として、Ag-Pd粉末を用いたのはNiメッキ膜を付け易くするためであり、無電解メッキ可能な金属であれば、Fe、Ni、Cu等の他の金属材料でも充分代替可能である。また金属粒子7は、樹脂6中に食い込んでいるため、アンカー効果により金属膜8の樹脂6への密着力を向上させる。

【0016】このようにして形成した突起電極は、樹脂

6の種類や塗布方法により高さをサブミクロンから任意に設定でき、さらにピッチもエッチング形成可能な大きさであるサブミクロン単位まで対応可能となる。さらに、突起電極中に樹脂6の層を含むため金属塊である従来技術の金属バンプ105に比べ容易に変形するため、前述したチップ・オン・ガラスと呼ばれる実装方法においては、平滑な基板上に突起電極を押圧することで確実な接続を取ることが出来る。一例をあげると、従来技術により形成した突起電極(図4)を持つ半導体素子と、本発明による突起電極を形成した半導体素子をチップ・オン・ガラス実装し比較したところ、従来技術では実装した半導体素子100個あたり接続不良が26/100発生したが、本発明による突起電極では接続不良は半導体素子100個あたり全く発生しなかった。

【0017】

【発明の効果】以上説明したように、本発明では、電極上に金属粒子を含む樹脂の層を形成し、電極および樹脂上に金属膜を形成することにより、微細なピッチでのバンプ形成が可能であり、さらに変形が容易に行えることにより平滑な基板への実装においても確実な接続を可能とする。さらに樹脂中に金属粒子を含有させることにより金属膜の形成を容易にし、金属粒子のアンカー効果により金属膜の樹脂への密着力を向上させ、高い信頼性を半導体装置に提供するものである。

【図面の簡単な説明】

【図1】本発明による一実施例を示す断面図である。

【図2】本発明による一実施例の要部を拡大して示した断面図である。

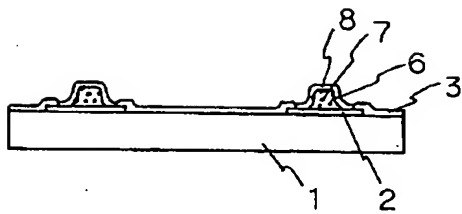
【図3】本発明による一実施例の製造工程を示した断面図である。

【図4】従来例を示す断面図である。

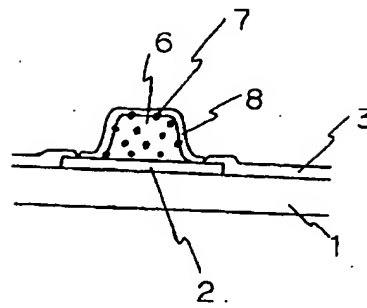
【符号の説明】

- 1 半導体素子
- 2 A1電極
- 3 パッシベーション膜
- 6 樹脂
- 7 金属粒子
- 8 金属膜
- 9 マスク
- 10 紫外線の照射方向を示す矢印
- 11 硬化した領域
- 12 パラジウム皮膜
- 101 半導体素子
- 102 A1電極
- 103 パッシベーション膜
- 104 バリアメタル
- 105 金属バンプ

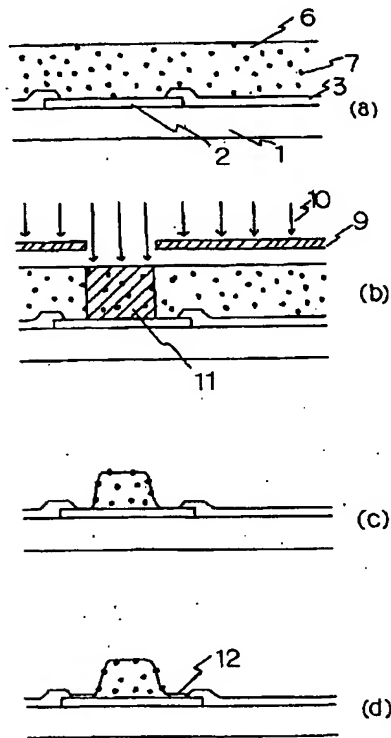
【図1】



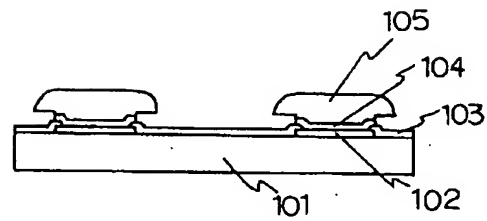
【図2】



【図3】



【図4】



PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SEIKO EPSON CORP

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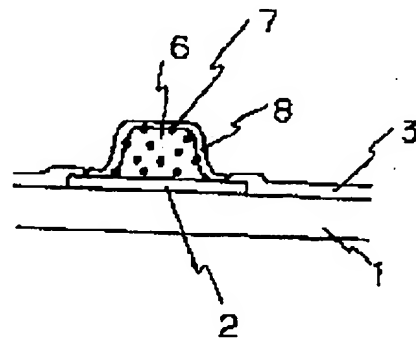
(72)Inventor : YAMAZAKI YASUO

(54) STRUCTURE AND FORMING METHOD OF PROTRUDENT ELECTRODE

(57)Abstract:

PURPOSE: To enable a protrudent electrode formed on an electronic element or a board to be improved in characteristics and enhanced in connection reliability when the electronic element is bonded facing downward.

CONSTITUTION: A resin 6 which contains metal particles 7 is formed on the Al electrode 2 of a semiconductor element 1. The semiconductor element 1 is dipped into a plating bath, the metal particles 7 protruding from the resin 6 serve as nucleuses to enable a metal film 8 to grow, whereby the metal film 8 is formed both on the resin 6 and on the AE electrode 2, and a protrudent electrode provided with a resin layer 6 is formed on the Al electrode 2. Therefore, bumps can be formed at a very small pitch. Furthermore, the metal particles 7 are contained in the resin 6, whereby the metal film 8 can be easily formed, and the metal film 8 is enhanced in adhesion to the resin 6 owing to the anchor effect of the mental particles 7, and in result a semiconductor of high reliability can be provided.



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CLAIMS

[Claim(s)]

[Claim 1] Structure of the projection electrode characterized by having formed the layer of the resin which distributed metal particles in the projection electrode with the configuration projected from the electrode on an electric element or a substrate so that the part on said electrode might be covered at least, and forming metallic coating only on said resin containing said metal particles, and said electrode.

[Claim 2] The formation approach of the process which forms the layer of the resin which distributed metal particles so that some electrodes on an electric element or a substrate might be covered, the process which forms a metallic film only on said resin layer which is immersed during an electroless deposition bath in said electric element or said substrate, and contains said electrode and said metal particles, and the projection electrode characterized by being a twist.

[Claim 3] Structure of the projection electrode according to claim 1 characterized by giving electroless deposition coats, such as nickel, Co, Cu, and Au, as the above-mentioned metallic film.

[Claim 4] Structure of the projection electrode according to claim 1 using the particle containing the metal in which electroless deposition, such as Au, nickel, Co, Pd, Cu, Zn, Sn, and Ag, is possible as the above-mentioned metal particles.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is concerned with the structure and the formation approach of a projection electrode which were formed on the electric element or the substrate, and relates to property amelioration of a projection electrode in more detail.

[0002]

[Description of the Prior Art] As an approach of forming a projection electrode, the projection electrode of a regulus was conventionally formed by the electroplating method.

[0003] Drawing 4 is the sectional view of the semiconductor device which has the projection electrode formed by the electroplating method. In drawing, the barrier metal in which aluminum electrode with which 101 was prepared in the semiconductor device and 102 was prepared on the semiconductor device 101, and 103 were formed on the aluminum electrode 102 by the passivation film, and 104 was formed with metals, such as nickel, Cr, and Pt, and 105 are metal bumps who achieve the duty of the projection electrode formed with electrolysis plating on the barrier metal 104.

[0004] Next, how to form a metal bump is explained. First, vacuum evaporatio~~no~~ formation of the metals, such as nickel, Cr, and Pt, is carried out by the spatter within a vacuum tub on a semiconductor device 101. The resist of a polyimide system is applied on the formed metal membrane, by irradiating ultraviolet rays on a mask in piles, the resist except the aluminum electrode 102 top is stiffened, solvent removal of the non-hardened resist is carried out, and only aluminum electrode top prepares opening. Next, the semiconductor device 101 in which the resist layer was formed is attached to Au plating bath, and an electrical potential difference is applied to a metal membrane. Only on the metal membrane exposed to opening of a resist, Au grows and the Au bump 105 is formed. After the Au bump 105 is formed, the barrier metal 104 is formed by carrying out solvent removal of the resist layer, using a bump 105 as a mask for a metal membrane further, and giving dry etching.

[0005]

[Problem(s) to be Solved by the Invention] By the above formation approaches of a projection electrode, it has the following troubles. That is, very many processes are complicated, the short-circuit between the terminals which adjoined in order that a manufacture unit price might become high since many processes which cost requires, such as vacuum deposition, are included, and a plated metal might grow also in the direction of a field of a semiconductor device occurs, and projection electrode formation of a detailed pitch is difficult. Moreover, in the approach of mounting the semiconductor device currently called the chip-on glass in the form of a face down on a substrate, connection dependability falls remarkably with the above-mentioned projection electrode with it difficult [to arrange height with homogeneity]. Since the above-mentioned projection electrode which is furthermore a regulus was not able to deform easily, the correspondence to a solid and smooth substrate was difficult for it.

[0006] This invention aims at offering the projection electrode corresponding to a detailed pitch that it was made that the above-mentioned technical problem should be solved, and is easy to deform on an electrode.

[0007]

[Means for Solving the Problem] Structure of the projection electrode by this invention is characterized by having formed the layer of the resin which distributed metal particles so that the part on said electrode might be covered at least, and forming metallic coating only on said resin containing said metal particles, and said electrode in a projection electrode with the configuration projected from the electrode on an electric element or a substrate.

[0008]

[Function] The resin containing metal particles is formed on an electrode. When a metal membrane grows by using as a nucleus the metal particles which were immersed in the metal plating bath and projected this from resin, a metal membrane is formed on resin, a metal membrane is formed also on an electrode at coincidence, and the projection electrode containing the layer of resin is formed on an electrode.

[0009]

[Example] Hereafter, one example by this invention is explained.

[0010] Drawing 1 is the sectional view of the semiconductor device which has a projection electrode by this invention, and drawing 2 is the sectional view having expanded and shown the important section of the projection electrode by this invention. The passivation film prepared in order that aluminum electrode prepared in order that 1 might perform a semiconductor device on a semiconductor device 1 and 2 might output and input an electrical signal, and 3 might protect the active side of a semiconductor device 1, the resin with which 6 was formed on aluminum electrode, the metal particles which distributed 7 in resin, and 8 are the metal membranes formed so that the resin 6 and aluminum electrode 2 top might be covered.

[0011] Drawing 3 (a) - drawing 3 (d) are the sectional views having shown the process which forms the projection electrode by this invention shown in drawing 1 and drawing 2, the arrow head with which 9 shows a mask and 10 shows the direction of radiation of ultraviolet rays, and 11 are the fields which resin 6 hardened by ultraviolet rays, and 12 is a palladium coat. The formation approach of the projection electrode by this invention is as follows.

[0012] First, optimum dose dropping of the resin 6 which distributed metal particles 7 uniformly is carried out using a dispenser etc. on the active side of a semiconductor device 1. In order to open the dropped resin 6 to homogeneity on a semiconductor device 1, high-speed rotation for 10 seconds is performed for a semiconductor device 1 by about 3,000 rpm, and the spin coat of the resin 6 is carried out so that it may become the thickness of about 20 micrometers. The resin 6 used at this time is polyimide system resin of a liquefied ultraviolet curing mold, and is making Ag-Pd powder with a particle size of 0.1-1 micrometer contain 5 to 20% in resin 6 as metal particles 7. having used the polyimide resin of an ultraviolet curing mold as resin 6 -- pattern formation -- easy -- it can carry out -- in addition -- and it is because it excels in chemical resistance, and as long as it is resin which is not invaded by electroless deposition liquid, film-like resin and nonphotosensitivity resin may be used. The semiconductor device 1 which carried out the spin coat of the resin 6 is dried at 80 degrees C for about 1 hour, and the structure of drawing 3 (a) is acquired. Next, as shown in drawing 3 (b), on the semiconductor device 1 of drawing 3 (a), alignment is carried out, the mask 9 which has opening in the location corresponding to the aluminum electrode 2 of a semiconductor device 1 is carried, ultraviolet rays are irradiated in the direction of an arrow head 10, and only a field 11 stiffens resin 6. By making opening of a mask 9 smaller than the aluminum electrode 2, the hardening field 11 of resin 6 is designed so that it may become smaller than the aluminum electrode 2.

[0013] In order to remove a part for the non-hard spot of resin 6, a semiconductor device 1 is immersed in the developer of resin 6 for about 2 minutes, and the structure of drawing 3 (c) is acquired. Since the hardening field 11 of resin 6 is also etched in part at this time, the thickness of resin 6 decreases 20 to 30% more from the condition which showed in drawing 3 (a). For this reason, as shown in drawing 3 (c), metal particles 7 will be in the condition of having projected from resin 6.

[0014] The palladium coat 12 activated on the aluminum electrode 2 as it was immersed in a tin (II) chloride solution and a palladium-chloride solution and a semiconductor device 1 was shown in drawing 3 (d) as pretreatment for plating also on the aluminum electrode 2 is formed.

[0015] In order to form a metal membrane 8 finally, a semiconductor device 1 is immersed in non-electrolyzed nickel plating bath. Since the palladium coat 12 exists on the aluminum electrode 2, nickel under electroless deposition bath deposits on the aluminum electrode 2 by permuting by the palladium coat 12. Moreover, the metal particles 7 projected from the front face of resin 6 on resin 6 are used as a nucleus, and nickel film grows. Thus, nickel film which grew on resin 6 by using metal particles 7 as a nucleus, and nickel film which grew on the aluminum electrode 2 join together, as shown in drawing 2, a metal membrane 8 is formed so that the aluminum electrode 2 and resin 6 may be covered, and a projection electrode is formed. As metal particles 7, if it is for making nickel plating film easy to attach and is the metal in which electroless deposition is possible, other metallic materials, such as Fe, nickel, and Cu, can be enough substituted for having used Ag-Pd powder. Moreover, since metal particles 7 are eating away into resin 6, they raise the adhesion force to the resin 6 of a metal membrane 8 according to an anchor effect.

[0016] Thus, the formed projection electrode can set height as arbitration from submicron one by the class and the method of application of resin 6, and correspondence of it is attained to the submicron unit which is further the magnitude that a pitch can also etching form. Furthermore, since it deforms easily compared with the metal bump 105 of the conventional technique which is a regulus since the layer of resin 6 is included in a projection electrode, in the mounting approach called the chip-on glass mentioned above, positive connection can be taken by pressing a projection electrode on a smooth substrate. Although the faulty connection occurred 26/100 per [which was mounted] 100 semiconductor devices with the conventional technique when an example was given, chip-on glass mounting was carried out and the semiconductor device with the projection electrode (drawing 4) formed with the conventional technique was compared with the semiconductor device in which the projection electrode by this invention was formed, in the projection electrode by this invention, the faulty connection hit 100 semiconductor devices and was not generated at all.

[0017]

[Effect of the Invention] As explained above, in this invention, by forming the layer of the resin containing metal particles on an electrode, and forming a metal membrane on an electrode and resin, bump formation in a detailed pitch is possible, and positive connection is enabled also in mounting to a smooth substrate by the ability deforming easily further. By making metal particles contain in resin furthermore, formation of a metal membrane is made easy, the adhesion force to the resin of a metal membrane is raised according to the anchor effect of metal particles, and a semiconductor device is provided with high dependability.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing one example by this invention.

[Drawing 2] It is the sectional view having expanded and shown the important section of one example by this invention.

[Drawing 3] It is the sectional view having shown the production process of one example by this invention.

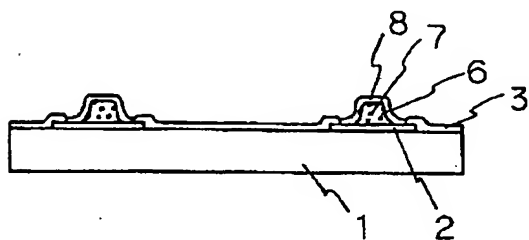
[Drawing 4] It is the sectional view showing the conventional example.

[Description of Notations]

- 1 Semiconductor Device
- 2 Aluminum Electrode
- 3 Passivation Film
- 6 Resin
- 7 Metal Particles
- 8 Metal Membrane
- 9 Mask
- 10 Arrow Head Which Shows Direction of Radiation of Ultraviolet Rays
- 11 Hardened Field
- 12 Palladium Coat
- 101 Semiconductor Device
- 102 Aluminum Electrode
- 103 Passivation Film
- 104 Barrier Metal
- 105 Metal Bump

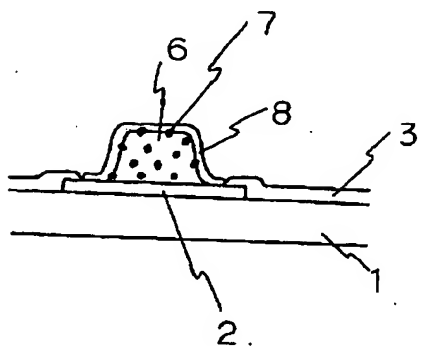
[Translation done.]

Drawing selection

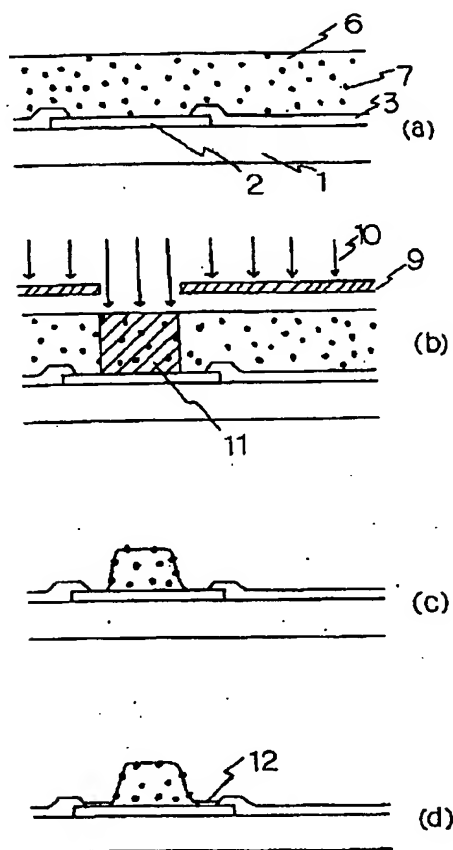


[Translation done.]

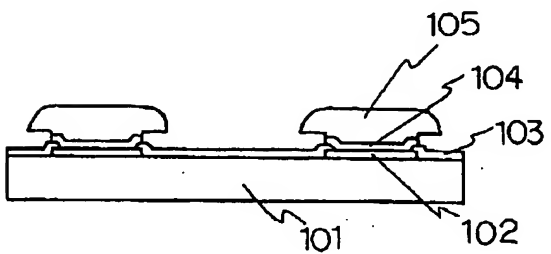
Drawing selection



[Translation done.]



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(54) 【発明の名称】 導電性ペースト

(57) 【要約】

【目的】 導電性が良好な導電性ペーストを提供する。

【構成】 直径1 μ m以下、長さ50 μ m以下の針状突起物を表面に有する金属粉と樹脂又は前記金属粉と樹脂と半導体粉からなる導電性ペースト。

【特許請求の範囲】

【請求項1】 樹脂と金属粉からなる導電性ペーストであって、金属粉が直径 $1\mu\text{m}$ 以下、長さ $50\mu\text{m}$ 以下の針状突起物を表面に有することを特徴とする導電性ペースト。

【請求項2】 樹脂と金属粉と半導体粉とからなる導電性ペーストであって、金属粉が直径 $1\mu\text{m}$ 以下、長さ $50\mu\text{m}$ 以下の針状突起物を表面に有することを特徴とする導電性ペースト。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、導電性が良好な導電性ペーストに関する。

【0002】

【従来の技術】樹脂と金属粉又は樹脂と金属粉と半導体粉からなる導電性ペーストは、この材料が持つ柔軟性のために電気工業、電子部品工業等の産業に多量に使用されている。このような導電性ペーストの成分のうち、金属粉又は金属粉と半導体粉が導電性に寄与し、樹脂が柔軟な接着性を保つために寄与している。そして導電性ペースト中に占める金属粉又は金属粉と半導体粉の割合が多い程、導電性ペーストの導電性が高くなるが、極端にその割合を多くすると導電性ペーストの接着性が損なわれる。このように導電性ペーストの導電性と接着性は反比例のような関係があるため、使用目的に応じて導電性ペーストの組成が決定されている。

【0003】

【発明が解決しようとする課題】導電性ペーストに使用される金属粉の形状は、通常球形であるが、前述したように、同一の接着性を保って少しでも導電性を高めるために、扁平形状とか楕円形状のものが提案され、実用に供されている。このような平板状の金属粉は、導電性ペースト中を電子が移動する場合に有利だと考えられているが、その機構については未だ明らかにされていない。しかしながら、このような新規な導電性ペーストにおいてもさらに導電性を高めたい用途には不向きであった。

【0004】

【課題を解決するための手段】本発明は、上記課題を達成すべくなされたもので、その要旨は金属粉が直径 $1\mu\text{m}$ 以下、長さ $50\mu\text{m}$ 以下の針状突起物を表面に有することを特徴とする導電性ペーストである。なお金属粉の一部を半導体粉に置換してもよい。

【0005】以下、本発明の導電性ペーストについて説明する。本発明において使用される樹脂としては、エポキシ樹脂、アルキッド樹脂、アクリル樹脂、フッ素樹脂、シリコン樹脂、フェノール樹脂、アリアル樹脂、炭化水素樹脂、セルロース樹脂等従来公知の樹脂が1種以上使用される。又、このような樹脂は、モノマー又はオリゴマーの形で1種以上使用し、最終的な導電性ペースト

トを使用した場合の硬化後に目的組成の樹脂になるものでも良い。

【0006】次に本発明において使用される金属粉としては、例えば、銀粉、金粉、パラジウム粉、銅粉、ニッケル粉、銀コートニッケル粉、銀コート銅粉およびこれらの合金等があげられ、2種以上使用しても良い。この中でもとりわけ銀粉、銀コートニッケル粉、銀コート銅粉が導電性が高いため望ましい。これら金属粉は、表面が針状突起物を有することが肝要である。

10 【0007】前記金属粉の表面が針状突起物を有するためには、金属粉表面を水洗して不純物イオンを除去した後乾燥し、さらにアルカリ洗浄、水洗、乾燥をくり返した後、 $40\sim 90^{\circ}\text{C}$ 、 $80\sim 90\%\text{RH}$ の恒温槽中で、数日 $\sim 2\sim 3$ 週間放置後、室温で乾燥することによって得られる。使用する金属粉の形状は、前述した球状、扁平状、楕円状いずれの形状であっても良い。本発明では、各金属粉表面の針状突起物の大きさは直径 $0.001\sim 1\mu\text{m}$ 、長さ $0.01\sim 50\mu\text{m}$ が好ましい。直径 $0.001\mu\text{m}$ 、長さ $0.01\mu\text{m}$ 以下では作製した導電性ペーストの導電性が十分でなく、直径 $1\mu\text{m}$ 、長さ $50\mu\text{m}$ を超えると作製した導電性ペーストの導電性の向上は顕著でなく、逆にコスト的に不利となり好ましくない。

20 【0008】また、使用する金属粉と樹脂との比率を適当に調節することにより所望の導電率を有する導電性ペーストが得られるが、ペースト中に占める金属粉の含量の好ましい割合は、 $20\sim 96$ 重量%である。金属粉の割合が 20 重量%未満ではペーストの導電性が不十分であり、又、 96 重量%を超えるとペーストの接着性が不十分であり、共に良好でない。

30 【0009】又、前述した金属粉は、一般に高価であるため、安価性を求める場合には金属粉の一部を半導体粉に置換してもよい。該半導体粉としては、電導度が $10^{-1}\text{s}\cdot\text{cm}^{-1}\sim 10^3\text{s}\cdot\text{cm}^{-1}$ の間にある半導体粉である。代表例として、二酸化マンガ、二酸化スズ、二酸化タングステン、二酸化鉛、二酸化チタン、一酸化銅、一酸化亜鉛、一酸化ニッケル、一酸化コバルト、三二酸化鉄、チタン酸バリウム、酸化タンタル、三二酸化バナジウム、三酸化タングステン、ポリチオフェン、ポリフラン、ポリピロール、ポリアニリン、ポリオキシベンゼン、ポリサルフィドベンゼン、ポリベンゼン、ポリベンゾピロリン、ポリピロリン、ポリカルバゾール、ポリフェノチアジン等が挙げられる。これらの半導体粉に適当な公知のドーバントを入れることにより電導度を調節して使用しても良い。

50 【0010】上述した導電性ペーストは、樹脂が溶解した適当な溶媒中に金属粉が分散した状態にあり、溶媒を除去して目的とする樹脂と金属粉又は樹脂と金属粉と半導体粉とからなる導電性ペーストとなる。又、樹脂自身が液体状のものは、前述した溶媒を使用しなくても良

く、乾燥硬化することによって固形の導電性ペーストとなる。

【0011】

【作用】金属粉が表面に針状突起物を有すると金属粉間の電子移動が針状突起物先端間を通して容易に行われるものと考えられる。

【0012】

【実施例】以下、実施例、比較例でもって本発明をさらに詳しく説明する。

実施例1～6、比較例1～6

粒径3～4 μ m、厚さ1 μ mの扁平銀粉を水洗し、50℃で減圧乾燥した。さらに2%KOH水溶液で洗浄した後、水洗し乾燥した。この操作を2回くり返した後60℃80%RHの恒湿槽に1週間放置した。このようにして得た金属粉は、針状突起物を表面に有し、その針状突起物は、径が平均0.03 μ m、長さが0.5 μ mであることを顕微鏡観察で確認した。表1は、このようにして得た銀粉を各種ポリマーに加えて導電性ペーストを作製した時の電導度を示した。尚、電導度は、ガラス板状に1mmの厚さで導電性ペーストを塗布し、極間距離1*20

*cmで測定した値である。又、各比較例は、各々の実施例で銀粉を前述した処理を行わない場合の導電性ペーストの電導度である。

【0013】実施例7～12、比較例7～12

粒径7 μ mの球状銀コートニッケル粉に実施例1と同様な処理で針状突起物を有する表面を形成した。針状突起物は径が平均0.01 μ m、長さ0.04 μ mであった。このような銀コートニッケル粉と、別に用意した各種の半導体粉と樹脂からなる導電性ペーストを作製し、電導度を測定し表2に示した。

【0014】実施例13～18

実施例2で銀粉を恒湿槽に放置する時間を変化させた以外は、実施例2と同様にして導電性ペーストを作製し、各例の電導度を測定し表3に示した。

【0015】比較例13

比較例2で作製した導電性ペーストを60℃80%RHの恒湿槽に1週間放置した後に乾燥して電導度を測定し、その値を表3に並記した。

【0016】

【表1】

	銀粉 wt %	樹脂		電導度 s \cdot cm ⁻¹
		種類	wt %	
実施例1	25	エポキシ	75	2 \times 10 ²
" 2	60	"	40	8 \times 10 ²
" 3	95	"	5	1 \times 10 ³
" 4	25	アクリル	75	1 \times 10 ³
" 5	60	"	40	5 \times 10 ³
" 6	95	"	5	7 \times 10 ³
比較例1	25	エポキシ	75	8 \times 10 ¹
" 2	60	"	40	1 \times 10 ²
" 3	95	"	5	3 \times 10 ²
" 4	25	アクリル	75	4 \times 10 ²
" 5	60	"	40	1 \times 10 ³
" 6	95	"	5	2 \times 10 ³

【0017】

※ ※ 【表2】

	銀粉コート ニッケル粉 wt %	樹脂	wt %	半導体粉	wt %	電導度 s \cdot cm ⁻¹
実施例7	20	アルキッド	60	二硫化鉛	20	1 \times 10 ²
" 8	50	"	30	"	20	4 \times 10 ²
" 9	70	"	10	"	20	5 \times 10 ²
" 10	20	フッ素	60	ポリビニール トルエンスル フオン酸ドー パント	20	3 \times 10 ²
" 11	50	"	30	"	20	7 \times 10 ²
" 12	70	"	10	"	20	1 \times 10 ³
比較例7	20	アルキッド	60	二硫化鉛	20	5 \times 10 ¹
" 8	50	"	30	"	20	8 \times 10 ¹
" 9	70	"	10	"	20	1 \times 10 ²
" 10	20	フッ素	60	ポリビニール トルエンスル フオン酸ドー パント	20	8 \times 10 ¹
" 11	50	"	30	"	20	2 \times 10 ²
" 12	70	"	10	"	20	4 \times 10 ²

【0018】

【表3】

	放置日数	針状突起物		電導度 $s \cdot cm^{-1}$
		径 μm	長さ μm	
実施例13	1	0.02	0.1	4×10^2
" 14	4	0.03	0.3	5×10^2
" 15	10	0.03	0.6	8×10^2
" 16	20	0.03	0.6	8×10^2
" 17	30	0.03	0.6	9×10^2
" 18	50	0.07	1.8	1×10^3
比較例13	—	なし		1×10^2

【0019】

【発明の効果】以上説明したように、本発明は、樹脂と
金属粉からなる導電性ペースト又は樹脂と金属粉と半導

10 体粉からなる導電性ペーストであって、金属粉が直径1
 μm 以下、長さ50 μm 以下の針状突起物を表面に有す
るので導電性が良好である。

【公報種別】特許法第 17 条の 2 の規定による補正の掲載

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【手続補正書】

【提出日】平成 13 年 10 月 29 日 (2001. 10. 29)

【手続補正 1】

【補正対象書類名】明細書

【補正対象項目名】特許請求の範囲

【補正方法】変更

【補正内容】

【特許請求の範囲】

【請求項 1】 樹脂と金属粉からなる導電性ペーストで

あって、金属粉が直径 1 μm 以下、長さ 50 μm 以下の針状突起物を表面に有することを特徴とする導電性ペースト。

【請求項 2】 樹脂と金属粉と半導体粉とからなる導電性ペーストであって、金属粉が直径 1 μm 以下、長さ 50 μm 以下の針状突起物を表面に有することを特徴とする導電性ペースト。

【請求項 3】 金属粉が、ペースト中に 20～96 重量 % 含有した請求項 1 または 2 に記載の導電性ペースト。

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(71)Applicant : SHOWA DENKO KK

(22)Date of filing : 17.04.1995

(72)Inventor : NAITO KAZUMI

(54) CONDUCTIVE PASTE

(57)Abstract:

PURPOSE: To provide good conductivity by forming specified needle-like projected parts on a metal powder.

CONSTITUTION: A conductive paste with a specified conductivity is obtained by properly adjusting the ratio of a metal powder having needle-like projected parts with $1\mu\text{m}$ or smaller in diameter and $50\mu\text{m}$ or shorter in length on the surface and a resin. As the metal powder, for example, silver, gold, palladium, copper, nickel, silver-coated nickel, silver-coated copper, and powder of alloys of these metals are preferable and two or more of them may be employed. Washing of the metal powder surface with water is carried out to remove ions of impurities and then drying is carried out, and further washing with an alkali and with water and drying are repeated. After that, the metal powders are kept still at $40-90^{\circ}\text{C}$ and $80-90\%\text{RH}$ (relative humidity) in a thermostat bath for several days to a couple of weeks to give metal powders having needle-like projected parts. A conductive paste having good conductivity can be obtained by producing the paste with the metal powder and resin such as epoxy resin, acrylic resin, etc.

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CLAIMS

[Claim(s)]

[Claim 1] The conductive paste which is a conductive paste which consists of resin and a metal powder, and is characterized by a metal powder having a needlelike projection with a diameter [of 1 micrometer or less], and a die length of 50 micrometers or less on a front face.

[Claim 2] The conductive paste which is a conductive paste which consists of resin, a metal powder, and semi-conductor powder, and is characterized by a metal powder having a needlelike projection with a diameter [of 1 micrometer or less], and a die length of 50 micrometers or less on a front face.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a conductive paste with good conductivity.

[0002]

[Description of the Prior Art] The conductive paste which consists of resin, a metal powder or resin and a metal powder, and semi-conductor powder is used for industries, such as electrician business and electronic-parts industry, so much for the flexibility which this ingredient has. Among such components of a conductive paste, a metal powder or a metal powder, and semi-conductor powder contributed to conductivity, and in order that resin may maintain a flexible adhesive property, it has contributed. And the conductivity of a conductive paste becomes high so that there are many rates of the metal powder or metal powder occupied during a conductive paste, and semi-conductor powder, but if the rate is extremely made [many], the adhesive property of a conductive paste will be spoiled. Thus, since the conductivity and the adhesive property of a conductive paste have relation like an inverse proportion, the presentation of a conductive paste is determined according to the purpose of use.

[0003]

[Problem(s) to be Solved by the Invention] Although the configuration of the metal powder used for a conductive paste is usually a globular form, as mentioned above, in order to maintain the same adhesive property and to raise conductivity, a flat configuration and elliptical thing is proposed and practical use is presented with it. Although it is thought that such a plate-like metal powder is advantageous when an electron moves under a conductive paste, it is not yet clear about the device. However, it was unsuitable for the application to raise conductivity further also in such a new conductive paste.

[0004]

[Means for Solving the Problem] This invention was made that the above-mentioned technical problem should be attained, and the summary is a conductive paste characterized by a metal powder having a needlelike projection with a diameter [of 1 micrometer or less], and a die length of 50 micrometers or less on a front face. In addition, a part of metal powder may be permuted by semi-conductor powder.

[0005] Hereafter, the conductive paste of this invention is explained. As resin used in this invention, one or more sorts of well-known resin, such as an epoxy resin, an alkyd resin, acrylic resin, a fluororesin, silicon resin, phenol resin, aryl resin, hydrocarbon resin, and cellulosic resin, is used conventionally. Moreover, such resin may turn into resin of the purpose presentation after hardening at the time of using one or more sorts in the form of a monomer or oligomer, and using a final conductive paste.

[0006] Next, as a metal powder used in this invention, silver dust, gold dust, palladium powder, copper powder, nickel powder, silver coat nickel powder, silver coat copper powder, these alloys, etc. are raised, and two or more sorts may be used, for example. It conflicts in this, and since reason silver dust, silver coat nickel powder, and silver coat copper powder of conductivity are high, it is desirable. As for these metal powders, it is important that a front face has a needlelike projection.

[0007] In order for the front face of said metal powder to have a needlelike projection, it dries, after rinsing a metal-powder front face and removing impurity ion, and after repeating alkali cleaning, rinsing, and desiccation further, it is obtained by drying at a room temperature after several days - 2-3 week neglect in the constant humidity chamber of 40-90 degrees C and 80 - 90%RH. the shape of the shape of the globular shape which mentioned the configuration of the metal powder to be used above, and flat, and an ellipse -- you may be which configuration. In this invention, the magnitude of the needlelike projection on each front face of a metal powder has the diameter of 0.001-1 micrometer, and desirable die length of 0.01-50 micrometers. The conductive improvement in the conductive paste produced when the conductivity of the conductive paste produced by the diameter of 0.001 micrometers and die length of 0.01 micrometers or less was not enough and exceeded the diameter of 1 micrometer and die length of 50 micrometers is not remarkable, and desirable. [become conversely disadvantageous in cost and]

[0008] Moreover, although the conductive paste which has desired conductivity by adjusting the ratio of the metal powder and resin to be used suitably is obtained, the rate that the content of the metal powder occupied during a paste is desirable is 20 - 96 % of the weight. If the conductivity of a paste has the inadequate rate of a metal powder at less than 20 % of the weight and it exceeds 96 % of the weight, the adhesive property of a paste is inadequate and it is not [both] good.

[0009] Moreover, since the metal powder mentioned above is generally expensive, when asking for cheap nature, it may permute a part of metal powder by semi-conductor powder. As this semi-conductor powder, electric conductivity is the semi-conductor powder between 10^{-5} second-cm -1 - 10^3 s-cm -1 . As an example of representation, a manganese dioxide, diacid-ized tin, a tungsten dioxide, a lead dioxide, a titanium dioxide, 1 oxidization copper, one zinc oxide, 1 nickel oxide, 1 cobalt oxide, an iron sesquioxide, barium titanate, tantalum oxide, a vanadium sesquioxide, a tungstic trioxide, the poly thiophene, Pori Fran, polypyrrole, the poly aniline, polyoxy benzene, polysulfide benzene, poly benzene, poly benzo pyrroline, poly pyrroline, the poly carbazole, the poly phenothiazin, etc. are mentioned. Electric conductivity may be adjusted and used by putting in the suitable well-known dopant for such semi-conductor powder.

[0010] The condition that the metal powder distributed in the suitable solvent which resin dissolved has the conductive paste mentioned above, and it turns into a conductive paste which consists of the resin which removes a solvent and is made into the purpose, a metal powder, or resin, a metal powder and semi-conductor powder. Moreover, it is not necessary to use the solvent with which resin itself mentioned the liquid-like thing above, and becomes a solid conductive paste by carrying out desiccation hardening.

[0011]

[Function] If a metal powder has a needlelike projection on a front face, it will be thought that the electronic transition between metal powders is easily performed through between needlelike projection tips.

[0012]

[Example] Hereafter, it is explained in more detail that this invention is also at an example and the example of a comparison.

Flat silver dust with a particle size [one to examples 1-6 and example of comparison 6 / of 3-4 micrometers] and a thickness of 1 micrometer was rinsed, and reduced pressure drying was carried out at 50 degrees C. After the KOH water solution washed 2 more%, it rinsed and dried. After repeating this actuation twice, it was left for one week in the constant humidity chamber of 60-degree-C80%RH. Thus, the obtained metal powder has a needlelike projection on a front face, and the needlelike projection checked by microscope observation that a path was [an average of 0.03 micrometers and die length] 0.5 micrometers. Table 1 showed the electric conductivity when adding the silver dust which carried out in this way and was obtained to various polymers, and producing a conductive paste. In addition, electric conductivity is the value which applied the conductive paste by the thickness of 1mm in the shape of a glass plate, and was measured by 1cm of distance between electrodes. Moreover, each example of a comparison is the electric

conductivity of the conductive paste when not performing processing which mentioned silver dust above in each example.

[0013] The front face which has a needlelike projection by the processing same into spherical silver coat nickel powder with seven to examples 7-12 and example of comparison 12 particle size of 7 micrometers as an example 1 was formed. The path of the needlelike projection was 0.04 micrometers in an average of 0.01 micrometers and die length. The conductive paste which consists of such silver coat nickel powder, semi-conductor powder of the various kinds prepared independently, and resin was produced, electric conductivity was measured, and it was shown in Table 2.

[0014] Except having changed the time amount which leaves silver dust in a constant humidity chamber in the 13 to example 18 example 2, the conductive paste was produced like the example 2, the electric conductivity of each example was measured, and it was shown in Table 3.

[0015] It dried, after leaving the conductive paste produced in the example 2 of example of comparison 13 comparison for one week in the constant humidity chamber of 60-degree-C80% RH, and electric conductivity was measured, and the account of the average of the value was carried out to Table 3.

[0016]

[Table 1]

	銀粉 wt %	樹 脂		電導度 $s \cdot cm^{-1}$
		種類	wt %	
実施例 1	25	エポキシ	75	2×10^2
" 2	60	"	40	8×10^2
" 3	95	"	5	1×10^3
" 4	25	アクリル	75	1×10^3
" 5	60	"	40	5×10^3
" 6	95	"	5	7×10^3
比較例 1	25	エポキシ	75	8×10^1
" 2	60	"	40	1×10^2
" 3	95	"	5	3×10^2
" 4	25	アクリル	75	4×10^2
" 5	60	"	40	1×10^3
" 6	95	"	5	2×10^3

[0017]

[Table 2]

	銀粉コート ニッケル粉 wt %	樹脂	wt %	半導体粉	wt %	電導度 $s \cdot cm^{-1}$
実施例 7	20	アルキッド	60	二酸化鉛	20	1×10^2
" 8	50	"	30	"	20	4×10^2
" 9	70	"	10	"	20	5×10^2
" 10	20	フッ素	60	ポリビロール トルエン スルホン酸 ドーパント	20	3×10^2
" 11	50	"	30	"	20	7×10^2
" 12	70	"	10	"	20	1×10^3
比較例 7	20	アルキッド	60	二酸化鉛	20	5×10^1
" 8	50	"	30	"	20	8×10^1
" 9	70	"	10	"	20	1×10^2
" 10	20	フッ素	60	ポリビロール トルエン スルホン酸 ドーパント	20	8×10^1
" 11	50	"	30	"	20	2×10^2
" 12	70	"	10	"	20	4×10^2

[0018]

[Table 3]

	放置日数	針状突起物		電導度 $\text{s} \cdot \text{cm}^{-1}$
		径 μm	長さ μm	
実施例13	1	0.02	0.1	4×10^2
" 14	4	0.03	0.3	5×10^2
" 15	10	0.03	0.6	8×10^2
" 16	20	0.03	0.6	8×10^2
" 17	30	0.03	0.6	9×10^2
" 18	50	0.07	1.8	1×10^3
比較例13	—	なし		1×10^2

[0019]

[Effect of the Invention] As explained above, this invention is a conductive paste which consists of the conductive paste or resin which consists of resin and a metal powder, a metal powder, and semi-conductor powder, and since a metal powder has a needlelike projection with a diameter [of 1 micrometer or less], and a die length of 50 micrometers or less on a front face, conductivity is good [this invention].

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[Method of Amendment] Modification

[Proposed Amendment]

[Claim(s)]

[Claim 1] The conductive paste which is a conductive paste which consists of resin and a metal powder, and is characterized by a metal powder having a needlelike projection with a diameter [of 1 micrometer or less], and a die length of 50 micrometers or less on a front face.

[Claim 2] The conductive paste which is a conductive paste which consists of resin, a metal powder, and semi-conductor powder, and is characterized by a metal powder having a needlelike projection with a diameter [of 1 micrometer or less], and a die length of 50 micrometers or less on a front face.

[Claim 3] The conductive paste according to claim 1 or 2 which the metal powder contained 20 to 96% of the weight during the paste.

[Translation done.]